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Ammonia synthesis at low temperatures

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Density functional theory (DFT) calculations of reaction paths and energies for the industrial and the biological catalytic ammonia synthesis processes are compared. The industrial catalyst is modeled by a ruthenium surface, while the active part of the enzyme is modeled by a MoFe_7S_9 complex. In contrast to the biological process, the industrial process requires high temperatures and pressures to proceed, and an explanation of this important difference is discussed. The possibility of a metal surface catalyzed process running at low temperatures and pressures is addressed, and DFT calculations have been carried out to evaluate its feasibility. The calculations suggest that it might be possible to catalytically produce ammonia from molecular nitrogen at low temperatures and pressures, in particular if energy is fed into the process electrochemically. © 2000 American Institute of Physics. [S0021-9606(00)70911-1]

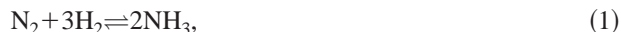
I. INTRODUCTION

The conversion of N_2 from the atmosphere into a biologically accessible form of nitrogen is a very difficult process. The formation of, e.g., NH_3 requires the N–N bond to be broken, and this bond is extremely strong, the bond energy being about 1000 kJ/mole. The process, therefore, requires either extreme temperatures, like in an arc, or the participation of an effective catalyst. Ammonia is synthesized from N_2 by two very different catalytic processes. Industrially it takes place by passing N_2 and H_2 over Fe or Ru surfaces at quite high temperatures and pressures, about 400 °C and 100 atm.^{1,2} In nature, on the other hand, the enzyme nitrogenase catalyzes the synthesis of ammonia from N_2 , electrons, and protons at room temperature and atmospheric pressure.^{3,4}

In the present paper we discuss why the two processes require such different reaction conditions, and whether a process similar to the biological one can be envisioned at a metal surface. We base the discussion on new insight into the molecular mechanisms of the two processes from experiments and from density functional calculations of the reaction energetics. The calculations suggest that a low temperature, low pressure process might be possible on a metal surface under certain conditions.

II. THE SURFACE PROCESS

The ammonia synthesis reaction,



on Fe and Ru surfaces has been the subject of a large number of experimental and theoretical studies and a detailed, molecular picture of the process has been developed.^{5–17} The reaction proceeds via dissociation of N_2 and H_2 on the surface with subsequent hydrogenation of the adsorbed N atoms. Our density functional theory (DFT) calculations of the reaction energetics on Ru surfaces illustrate the reaction

mechanism, see Fig. 1. The dissociation of N_2 is the rate limiting step in this reaction. The barrier for dissociation is rather low; experiments find a dissociation barrier close to zero on Fe surfaces^{7,8} and as low as 40 kJ/mole on stepped Ru.⁹ Both values are consistent with the temperature dependence of the synthesis rate measured on an industrial catalyst.^{10–15} They are also in excellent agreement with reaction barriers calculated using DFT.^{9,16} The high temperatures and pressures are, therefore, not needed for N_2 dissociation to take place. H_2 dissociation is even more facile.^{10,17} The problem in the surface process is that the bonding of the N and H atoms to the metal surfaces is so strong (cf. Fig. 1) that high temperatures are needed to have enough clean, reactive surface available for dissociation and reaction.^{12,13} The high temperature has the side effect that the equilibrium in Eq. (1) is shifted to the left. This is not desirable, since no catalyst can produce more ammonia than the equilibrium amount. The high pressures are chosen to alleviate this problem, since that shifts the equilibrium back towards the products again.

A low temperature process based on N_2 and H_2 dissociation on the catalyst surface would, therefore, require a surface which does not bind the N and H atoms too strongly while keeping the barrier for N_2 dissociation low. Ru may be a slightly better catalyst than Fe because it does that to some extent, but a really good, low temperature catalyst based on the reaction Eq. (1) may be hard to find because the N-surface bond strength and the barrier for N_2 dissociation tends to be strongly coupled so that a weaker N-surface bond also results in a higher dissociation barrier.^{18,19}

III. THE ENZYME PROCESS

The enzyme nitrogenase represents an alternative catalyst for the ammonia synthesis. The active part in the enzyme is believed to be the FeMo cofactor (FeMoco) which has the stoichiometric formula MoFe_7S_9 (homo-citrate). The overall process can be written

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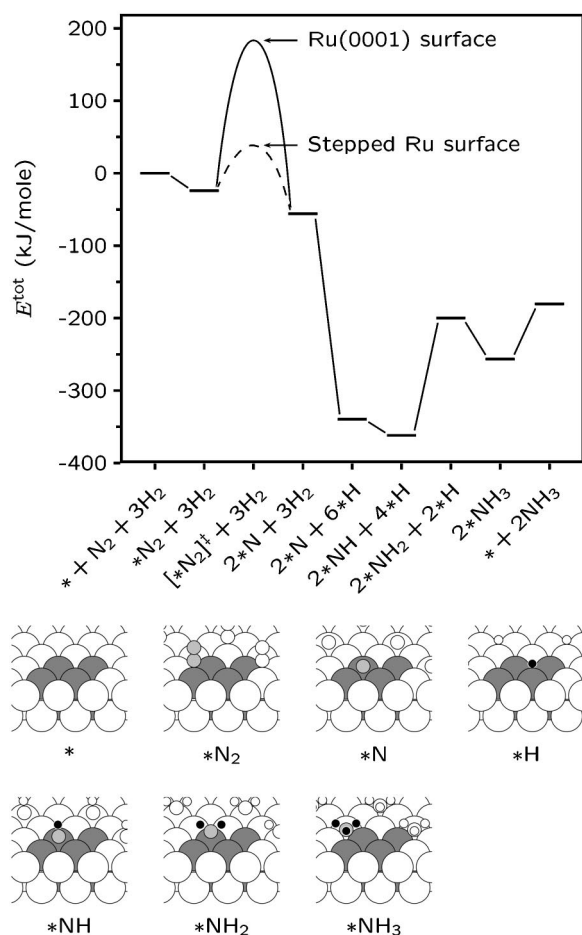


FIG. 1. Energy diagram for ammonia synthesis on Ru(0001). In the top panel the calculated energies for intermediates of the ammonia synthesis on Ru(0001) are shown, together with the calculated barriers for N_2 dissociation on a Ru(0001) surface and on stepped Ru surface. For the barrier see Ref. 9 for further details. The binding energy is defined relative to the energies of the free Ru(0001) surface ($*$), and the gas phase molecules $\text{N}_{2(g)}$, and $\text{H}_{2(g)}$ by $E^{\text{tot}} = E(X) - E(*) - E(\text{N}_{2(g)}) - 3E(\text{H}_{2(g)})$, where X denotes the species shown along the horizontal axis. Structures of the most stable intermediates are shown below the energy diagram. One super cell is gray toned such that Ru is medium gray, N is light gray, and H is black.



where the obligatory simultaneous H_2 evolution has been left out. The electrons are provided by reduced ferredoxin. Large amounts of energy is used in the process, both in the form of a high chemical potential of the electrons and in the form of hydrolysis of at least 16 molecules adenosinetriphosphate (ATP) per turn over of Eq. (2).^{3,4}

The active site of the enzyme is very well characterized,^{20–32} but the detailed molecular mechanism is not as well established as for the metal surface process. It is generally believed that the biological process does not involve initial breaking of the N–N bond,³³ and recent DFT calculations on different Mo, Fe sulfide complexes modeling the FeMoco^{34–36} support this picture. These are the same type of calculations,^{9,16} describing in detail the experimentally very well characterized surface process. It is, therefore, likely that the approach can be used to describe the enzyme process as well. Here the main approximation is that only a small fraction of the enzyme can be included. DFT calcula-

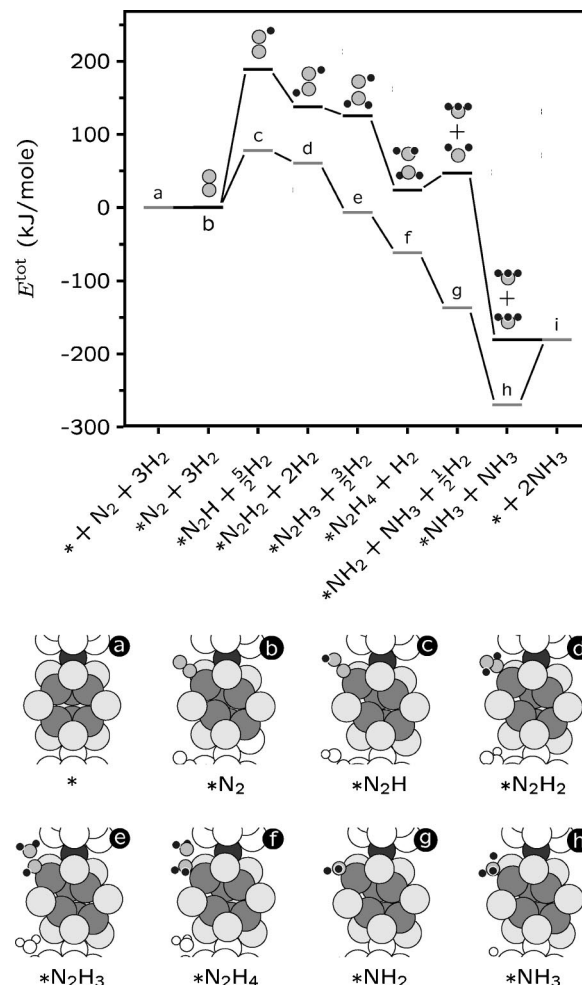


FIG. 2. Energy diagram for the hydrogenation of N_2 in the gas phase and on the MoFe_6S_9 complex modeling the FeMoco. In the top panel the calculated binding energies of the most stable intermediates along the reaction path for hydrogenation of N_2 on the MoFe_6S_9 complex (gray bars) and in the gas phase (black bars) are plotted. The binding energy, E^{tot} , defined in Fig. 1, is relative to the gas phase molecules $\text{N}_{2(g)}$ and $\text{H}_{2(g)}$. The asterisk along the horizontal axis denotes either the MoFe_6S_9 complex in case of the gray bars or vacuum in case of the black bars. The labels of the gray bars refer to the most stable intermediates of the complex shown below the energy diagram with one super cell gray toned. The gas phase structures are shown immediately above the corresponding black energy bars. The calculations for the gas phase is in reasonable agreement with Refs. 35 and 56 and references therein. One super cell is gray toned with the key: Light gray large circles: S; medium gray: Fe; dark gray: Mo; light gray small circles: N; and black: H.

tions using a MoFe_6S_9 complex to model the FeMoco suggest that N_2 is adsorbed on the FeMoco without dissociating, and when electrons and protons are added to the N_2 molecule one by one, first one and then the second NH_3 molecule (or NH_4^+ ion) leaves the catalytic site.³⁶ Figure 2 compares the energetics of adding H atoms (from H_2) to an N_2 molecule in the gas phase and adsorbed on the MoFe_6S_9 complex. The effect of the MoFe_6S_9 complex is very significant, in particular in stabilizing the least stable NNH intermediate by 110 kJ/mole.

The calculated energetics, Fig. 2, suggests that if the hydrogen entering the process comes directly from H_2 , the model enzyme still has a sizeable “barrier” associated with the NNH intermediate. In the biological process H_2 is not the

source of hydrogen atoms, and the energy of the (H^+) entering Eq. (2) is different from that of hydrogen in H_2 . It may be³⁶ that the reaction is able to proceed at room temperature because the enzyme feeds hydrogens with a higher chemical potential than in H_2 into the reaction in the form of electrons with a high electrochemical potential and/or through the hydrolysis of ATP.^{4,37–39} If this is the case, it might be possible to produce ammonia by electrolysis of the isolated FeMoco. So far no one has been able to do that, but a first step in this direction has been taken by Pickett *et al.*²⁵ who have reported that for large enough negative bias, H_2 can be produced, showing that the chemical potential of ($\text{H}^+ + e^-$) in the active site of the enzyme can be raised electrochemically above that of hydrogen in H_2 . Shilov *et al.*⁴⁰ have catalytically reduced acetylene by means of the FeMoco and various amalgams as reductants. In this connection it is also relevant to note that there has been several reports on the protolysis of N_2 containing transition metal complexes under strongly reducing conditions.^{41–43}

The possibility that we will discuss in the following is whether a process like the one shown in Fig. 2 is possible directly on a metal surface in particular if extra energy is fed into the reaction electrochemically. We are using the DFT calculations to study the question whether the FeMoco model system we consider is unique in letting the process in Fig. 2 go so relatively easily, or whether a similarly facile process is possible at a metal surface. If that is the case, it might be possible to form NH_3 at a metal surface, by using it as the cathode in a proton containing electrolyte in the presence of molecular nitrogen.

IV. CALCULATIONAL DETAILS

The DFT calculations behind the results in Figs. 1 and 2 and the further results to follow are based on a plane-wave expansion of the wave functions, a GGA description of exchange and correlation effects,^{44,45} and ultra soft pseudopotentials⁴⁶ except for S where a nonlocal soft pseudopotential⁴⁷ is used. Plane waves with kinetic energies up to 25 Ry are used. The self-consistent electron density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi-population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density.⁴⁸ All total energies have been extrapolated to $k_B T = 0$ eV.

In the DFT calculations, the MoFe_6S_9 complex is repeated periodically in one direction to give all Fe and Mo atoms the same coordination number as in the real FeMoco. In the other two directions the system is also repeated periodically but with vacuum in between to avoid interaction effects. A complete structural relaxation to the lowest energy state is performed for each configuration studied. It turns out that the model MoFe_6S_9 complex has bond lengths and angles closely resembling those found experimentally for the FeMoco.^{27–32} For further details of the calculations on the model of the active part of the enzyme, see Ref. 36. The only difference is that in the present paper the obtained densities are used as input for a total energy calculations using the

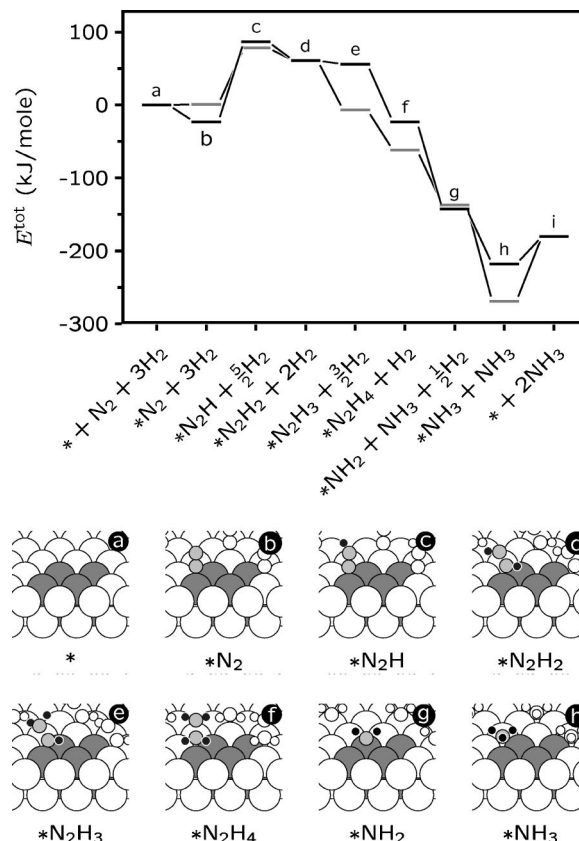


FIG. 3. Energy diagram for the hydrogenation of N_2 on the Ru(0001) surface and on the MoFe_6S_9 complex modeling the FeMoco. In the top panel the binding energies of the most stable intermediates for the adsorption and hydrogenation of N_2 are plotted for Ru(0001) (black bars) and the MoFe_6S_9 complex (gray bars). The total binding energy, E_{tot} , defined in Fig. 1, is relative to the gas phase molecules $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$. The asterisk along the horizontal axis denotes either the MoFe_6S_9 complex in case of the gray bars or the Ru(0001) surface in case of the black bars. The labels of the black bars refer to the structures of the most stable intermediates for the Ru(0001) surface shown below the energy diagram. One super cell is gray toned such that Ru is medium gray, N is light gray, and H is black.

slightly more accurate RPBE functional to describe exchange correlation effects.⁴⁵

The metal surface chosen to study the question of a molecular N_2 hydrogenation process is the Ru(0001) surface modeled by a periodic array of two layer slabs separated by the equivalent of five layers of vacuum. An unit cell giving (2×2) periodicity along the surface is used and the corresponding Brillouin zone is sampled by 18 special k -points. The two layer slab gives results for N and N_2 adsorption that are within 0.2 eV of the results using 3–6 layers. The remaining computational details are exactly as for the model enzyme.³⁶ The adsorbed species were allowed to fully relax, but the substrate atoms were kept fixed at their ideal bulk positions.

V. GENTLE N_2 HYDROGENATION

In Fig. 3 we investigate the possibility of hydrogenating N_2 directly when it is adsorbed on the Ru(0001) surface. As for the MoFe_6S_9 complex the calculations for the surface have been performed by first adsorbing N_2 and then adding

H atoms one by one. Each time a new H atom is added several bindings sites on N_2 have been tried in order to find the most stable intermediate. In Fig. 3 we include the structures of the most stable intermediates.

It is clear from Fig. 3 that the most stable intermediates on the Ru surface are very similar to those found for the model enzyme. In both cases the first hydrogenation step is endothermic. After that the reaction proceeds exothermically until the first ammonia splits off after addition of the fifth hydrogen, Fig. 3(g). Addition of the sixth hydrogen forms adsorbed ammonia Fig. 3(h), which desorbs endothermically, Fig. 3(i).

In agreement with other evidence,^{49,50} our calculations indicate that the transfer of protons to the adsorbed N_2 is not associated with significant energy barriers. If we assume this to be the case, the rate limiting step is associated with reaching the state Fig. 2(c) or Fig. 3(c). The small adsorption energy, $E(b)$, gives rise to a low coverage of N_2 at the temperatures and pressures of interest here (300 K and 1 atm). It is simple to show that due to the low coverage, the rate for the total reaction depends only on $E(c)$ and not on $E(c) - E(b)$.⁵¹ The overall activation energy for the total reaction is, therefore, equal to $E(c)$. We find $E(c) = 80$ kJ/mole for the $MoFe_6S_9$ complex and $E(c) = 90$ kJ/mole for Ru(1001). As discussed above, when the hydrogen atoms are added in the form of electrons and protons, the barrier may be decreased by changing the electrochemical potential of the electrons.

The calculations do not have an accuracy to predict accurately activation energies, but they strongly indicate that for a sufficiently negative bias the metal surface should in principle allow ammonia production at room temperature and atmospheric pressure. There are of course a number of potential problems in achieving this, the most serious of which may be the competition of the ammonia synthesis with hydrogen evolution. The same is seen in the enzyme process where H_2 production also competes with NH_3 formation. On the Ru surface the problem is worse because H atoms bind stronger than N_2 to the surface, while the opposite is true at the active site of the $MoFe_6S_9$ complex, where H bound to Fe is unstable relative to H on S or $H_{2(g)}$.³⁶ Perhaps steps which bind N_2 significantly stronger than terraces and does not bind H atoms quite as strongly can act as active sites for this reaction. This may, however, introduce N_2 dissociation which would immediately destroy the reactive sites. Alternatively, the Ru surface or other metal surfaces may have to be poisoned by, e.g., sulfur adsorption which both prevents H adsorption⁵² and N_2 dissociation.⁵³ In fact, one may view the FeMoco as a Fe cluster passivated by S. In this connection it may be important that the cluster can distort to accommodate the N_2 , see Fig. 2(a) and 2(b), as pointed out by Somorjai and Borodko.⁵⁴ Yet another possibility is to use a noble metal or a surface alloy adsorbing H atoms less strongly.

Apart from a negative bias, the requirement for a low temperature ammonia synthesis reaction from N_2 is that protons are readily available. This may be accomplished in solution, or by using a proton conductor as the electrolyte. It cannot be excluded that the enzyme has a structure that facilitates the proton transfer particularly well, and that it is

difficult to obtain equally good conditions at a metal surface. On the other hand, it is known that even the isolated cofactor can produce H_2 ,²⁵ can protonate acetylene,⁴⁰ and binds CO in much the same way as in the enzyme.²⁶

Recently it has been reported that ammonia was produced electrochemically by a Pd catalyst on a proton conducting oxide.⁵⁵ We suggest that this might have happened by the mechanism discussed here. We note that a reasonably low temperature reaction using H_2 as the H source might even be possible at the surface if N_2 dissociation and H poisoning can be avoided.

VI. SUMMARY

In summary, we have calculated the most stable intermediates along a reaction path where adsorbed N_2 on Ru(0001) is hydrogenated, and compared the results with the corresponding reaction mechanism previously published for the enzyme nitrogenase. The comparison shows many similarities between the mechanism on these two catalysts. In particular, we find that both reaction mechanism may proceed at low temperature if hydrogen is fed into the reaction in the form of electrons and protons with a higher chemical potential than hydrogen in the form of H_2 .

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